Anthracene Derivatives as Acceptors of the Reaction Intermediate Generated by the Decomposition of Tropone Tosylhydrazone Sodium Salt. Regioselective Cycloaddition Reactions of Cycloheptatrienylidene or 1,2,4,6-Cycloheptatetraene with 9-Substituted Anthracene Derivatives

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The rearrangement of the carbene, cycloheptatrienylidene, to the allene, 1,2,4,6-cycloheptatetraene, was investigated. Tropone tosylhydrazone sodium salt, the precursor of cycloheptatrienylidene was decomposed in the presence of various kinds of 9-substituted anthracene derivatives to afford cycloaddition products, whose structures show that the carbenic carbon atom or the allenic carbon atom of the carbene or the allene attacks the carbon atoms at the 10-position of the anthracenes. It is obvious that the electronic natures of the substituents on the anthracenes have no effect on the regioselectivity of the addition reaction, suggesting that the reaction proceeds via 1,2,4,6-cycloheptatetraene, which is derived from the cycloheptatrienylidene initially generated from the tosylhydrazone.

The structure of the nucleophilic singlet carbene, cycloheptatrienylidene (**2**), is considered to be the 6π-electron aromatic structure (**2a**) bearing the divalent carbenic carbon atom of sp^2 hybridization (**2b**).[1] The experimental facts that **2** adds to maleonitrile and fumaronitrile with stereospecificity[1b,c] and that the relative rate constants of the addition reaction of **2** with styrene derivatives correlate well with the Hammet equation ($\rho=+1.05$)[1d] prove the singlet and the nucleophilic natures of **2** respectively.

Recently, the possibility of interconversion between **2** and the allene, 1,2,4,6-cycloheptatetraene (**4**), which has a twisted structure bearing the sp hybridized allenic carbon atom (**4a**), has attracted the attention of chemists, and a number of papers have been published.[2] One of them says that **2** does not represent an energy minimum; instead, it is the transition state for the interconversion of enantiometric allenes.[2d,g,h] Previously, the present authors reported an example of the rearrangement of **2** to **4**, in connection with the [4+2]-type cycloaddition reactions of **2** with a variety of enophiles.[2c,e,f] We have now examined the reaction of **2** with various kinds of 9-substituted anthracene derivatives in order to get additional evidence on the rearrangement with the expectation that, if the reaction proceeds via the nucleophilic carbene **2**, the introduction of the electron-donating or the electron-attracting substituents on anthracene will affect the regioselectivity or the product yields of the reaction. Here the result of these reactions will be reported.

Results and Discussion

When tropone tosylhydrazone sodium salt (**1**) was decomposed at 125 °C for 15 min in anhydrous diglyme in the presence of one molar equivalent of the anthracene derivatives (**5a—g**), the respective adducts (**6a—g**) were obtained together with quantitative amounts of nitrogen gas and sodium *p*-toluenesulfinate (**3**). The yields, the chemical shifts, and the coupling constants in the NMR spectra of the adducts are summarized in the table.

The structures of the adducts were determined on the basis of their physical properties and confirmed by a comparison of the spectral properties, especially the NMR spectral properties, with those of the analogous compounds.[2e,3] The singlet signals due to the methine proton (H_a) in the NMR spectra definitely show the arrangement of the double bonds in the cycloheptatriene moiety of the adducts, showing the regioselectivity of the reaction.

These structures of the adducts show that the carbenic carbon atom of **2** or the allenic carbon atom of **4** selectively attacks the carbon atoms at the 10-position of the anthracene derivatives.

Two possible mechanisms may be thought of for

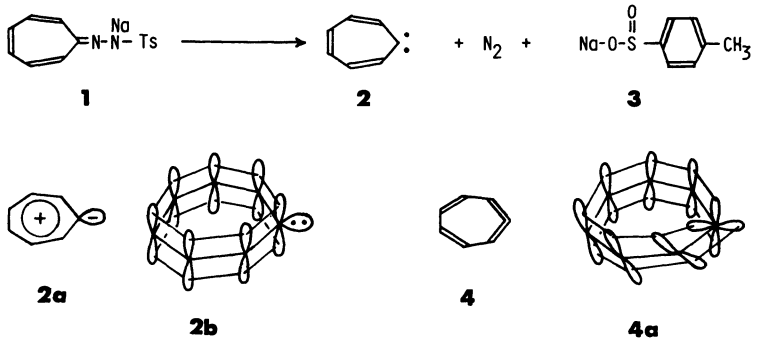

Fig. 1.

the reaction. Pathway A includes the carbene intermediate **2**, which reacts with **5** to afford the tropylium cation intermediate (**7**). Subsequent cyclization reaction of the intermediate leads to the formation of **6**. Closer examination into Pathway A, however, reveals that it does not adequately explain the observed products. That the intermediate **2** is proved to be a nucleophilic carbene; therefore, it seems reasonable that the carbenic carbon atom of **2** attacks the electron-deficient carbon atoms at the 10-position of **5b—g**, which have electron-withdrawing groups, to give the observed adducts, **6b—g**, via the intermediates **7b—g**. However, as for the other substance, anthracene **5a**, which has the electron-donating group, the carbenic carbon atom of **2** should attack the carbon atom at the 9-position to give the imaginary adducts **8a**, for in this anthracene the electron density at the 9-position is less than that at the 10-position. The experimental result shows that the attacking positions are the same at the 10-position for all of the **5**, without distinction of the electronic natures of the substituents. The lack of any obvious effect on the product yields by the electronic natures of the substituents also seems to suggest that the reaction does not proceed via **2**.

Table 1. Yields and NMR Spectral Data of the Adducts

No	6a	6b	6c	6d	6e	6f	6g
X	CH_3	Ph	Cl	Br	$COCH_3$	CN	NO_2
Yield	15%	4%	8%	12%	14%	8%	25%
NMR spectral data*							
H_a (s)	4.82	4.90	4.82	4.82	4.82	4.83	4.83
H_b (d) J_{bc}=5	1.95	2.64	2.55	2.61	2.67	2.59	2.97
H_c (dd) J_{bc}=5, J_{cd}=10	4.52	4.53	4.79	4.76	4.48	4.68	4.57
H_d (d) J_{cd}=10	5.90	5.91	5.96	5.96	5.94	5.81	5.91
H_e H_f (m) H_g	6.25	6.24	6.24	6.24	6.31	6.10	6.25
CH_3 (s)	2.03				2.60		
Ph (m)	6.9—7.5 (8H)	6.9—7.5 (13H)	7.0—7.8 (8H)	7.0—7.8 (8H)	7.0—7.5 (8H)	6.9—7.8 (8H)	7.0—7.5 (8H)

* Chemical shifts in δppm and coupling constants in Hz.

Pathway B involves the rearrangement of **2** to the allene intermediate **4**. Allenes are known to proceed radical-type reactions.[4] The radical-type attack of the allenic carbon atom of **4** on the carbon atom at the 10-position of **5** gives the diradical intermediate **9**, which then cyclizes to form **6**. When the allenic carbon atom attacks the 9-position carbon of **5**, the imaginary adduct **8** might be formed via the diradical intermediate **10**. It is, however, obvious that the diradical intermediate **9** is more stable than **10**; therefore the preferential product should be **6**.

The facts that some carbenes are known to rearrange to the corresponding allenes,[5] and that anthracenes are active acceptors in addition reactions with allenes,[6] seem also to support the estimation that these reac-

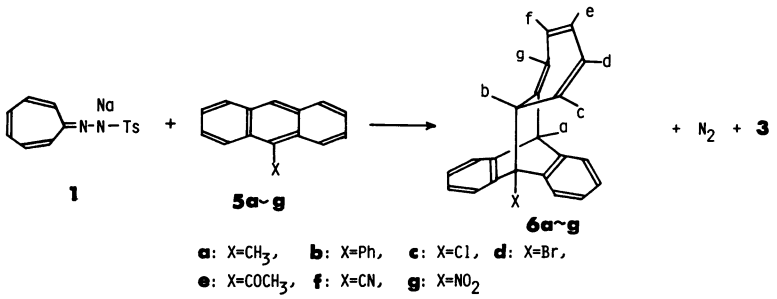

Fig. 2.

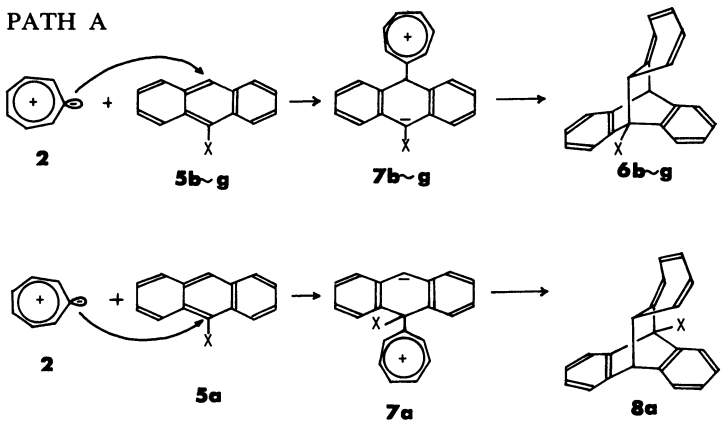

Fig. 3.

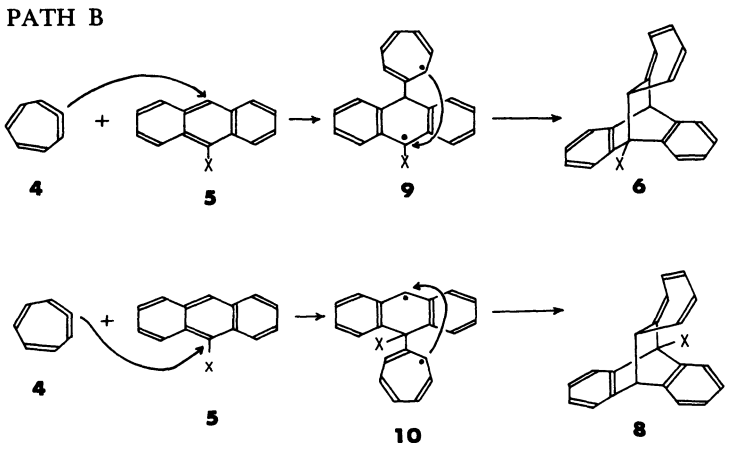

Fig. 4.

tions are addition reactions between the anthracene derivatives and the allene intermediate **4**.[7]

Experimental

All the melting and boiling points are uncorrected. The NMR spectra were measured with a Hitachi R-20B or a Varian XL 200 spectrometer, with tetramethylsilane as the internal standard. The mass spectra were recorded with a Hitachi M-52 or a JMS-DX300 spectrometer. The UV and IR spectra were measured with Hitachi 220A and DS-701G spectrometers respectively. Wako gel C-200 and Wako gel B5-F were used for the column and thin-layer chromatography respectively. The diglyme was dried over Molecular Sieves 3A 1/16.

Reaction of 1 with 5a. A mixture of **1** (14.80 g, 50 mmol), **5a** (9.60 g, 50 mmol), and anhydrous diglyme (100 ml) was heated at 120 °C for 15 min. After the evolution of a quantitative amount of nitrogen gas had ceased (1.1 l), a quantitative amount of a brown powder of **3** (8.85 g) was removed by filtration. The filtrate was diluted with ether, washed several times with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to give a tarry material, which was chromatographed on silica gel to give crystals of the recovered **5a** (7.44 g) when pet ether was used and yellow crystals **6a** (1.65 g, 12%) by the use of pet ether–benzene (9:1). Recrystallization from benzene gave pure **6a**.

6a: Mp 134—135 °C. Found: *m/z* 283.1404. Calcd for $C_{22}H_{18}$: 283.1417. Mass *m/z* (rel intensity): 283 (M^+, 96), 267 (52), 192 (100). IR (KBr): 3020, 2950, 1460, 1380 cm^{-1}. UV (EtOH): 273 nm (log ε, 3.70).

Reaction of 1 with 5b. A mixture of **1** (14.80 g, 50 mmol), **5b** (12.70 g, 50 mmol), and anhydrous diglyme (100 ml) was heated at 120 °C for 15 min to evolve a quantitative amount of nitrogen gas (1.1 l). After the removal of **3** (8.60 g, 97%) by filtration, the filtrate was treated as usual to give a mixture of crystals and an oil. The crystals of the recovered **5b** (11.13 g) were removed by filtration, and the filtrate was chromatographed on silica gel to yield a pale yellow oil **6b** (0.67 g, 4%) by the use of pet ether–benzene (8:2). The oil **6b** was further purified by thin-layer chromatography on silica gel, using pet ether–benzene (9:1) as the developing solvent (R_f=0.75).

6b: Found: *m/z* 344.1568. Calcd for $C_{27}H_{24}$: 344.1564. Mass (rel intensity): 344 (M^+, 100), 268 (13), 253 (60). IR (oil): 3020, 2950, 1160, 1460 cm^{-1}. UV (EtOH): 253 nm (log ε, 3.66).

Reaction of 1 with 5c. A mixture of **1** (14.80 g, 50 mmol), **5c** (10.65 g, 50 mmol), and anhydrous diglyme (100 ml) was heated at 120 °C for 15 min to evolve a quantitative amount of nitrogen gas (1.1 l). After the separation of **3** (8.13 g, 91%) by filtration, the filtrate was treated as usual to give a mixture of crystals and an oil. The crystals of the recovered **5c** (2.81 g) were removed by filtration, and the filtrate was chromatographed on silica gel to give crystals of the recovered **5c** (6.46 g) when pet ether was used and a pale yellow oil **6c** (1.17 g, 8%) when pet ether–benzene (9:1) was used. The oil **6c** was further purified by thin-layer chromatography, using pet ether–benzene (9:1) as the developing solvent (R_f=0.40).

6c: Found: *m/z* 302.0839. Calcd for $C_{21}H_{15}Cl$: 302.0861. Mass *m/z* (rel intensity): 302 (M^+, 55), 267 (90), 252 (36), 212 (100). IR (oil): 3040, 2950, 1460 cm^{-1}. UV (EtOH): 275 nm (log ε, 3.91).

Reaction of 1 with 5d. A mixture of **1** (14.80 g, 50 mmol), **5d** (12.90 g, 50 mmol), and anhydrous diglyme (100 ml) was heated at 120 °C for 15 min to evolve a quantitative amount of nitrogen gas (1.1 l). After the separation of **3** (8.85 g, 99%) by filtration, the filtrate was treated as usual to give a mixture of crystals and an oil. The crystals of the recovered **5d** (7.30 g) were removed by filtration, and the filtrate was chromatographed on silica gel to give crystals of the recovered **5d** (4.10 g) when pet ether was used and a yellow oil **6d** (2.15 g, 13%) when pet ether–benzene (8:2) was used. The oil **6d** was further purified by thin-layer chromatography on silica gel, using pet ether–benzene (8:2) as the developing solvent (R_f=0.60).

6d: Found: *m/z* 346.0355. Calcd for $C_{21}H_{15}Br$: 346.0375. Mass *m/z* (rel intensity): 348 (M^+, ^{81}Br, 65), 346 (M^+, ^{79}Br, 69), 268 (100), 259 (43), 257 (43). IR (oil): 3030, 2960, 1450 cm^{-1}. UV (EtOH): 273 nm (log ε, 3.84).

Reaction of 1 with 5e. A mixture of **1** (14.80 g, 50 mmol), **5e** (11.00 g, 50 mmol), and anhydrous diglyme (100 ml) was heated at 120 °C for 15 min to evolve a quantitative amount of nitrogen gas (1.1 l). After the separation of a quantitative amount of **3** (8.90 g) by filtration, the filtrate was treated as usual to give a tarry material, which was then chromatographed on silica gel to give a yellow oil **6e** (2.11 g, 14%) when pet ether–benzene (7:3) was used and crystals of the recovered **5e** (6.91 g) when pet ether–benzene (6:4) was used. The oil **6e** was further purified by

thin-layer chromatography, using pet ether–benzene (7:3) as the developing solvent (R_f=0.60).

6e: Found: *m/z* 310.1350. Calcd for $C_{23}H_{18}O$: 310.1356. Mass *m/z* (rel intensity): 310 (M^+, 31), 267 (100), 220 (28), 205 (52). IR (oil): 3030, 2950, 1710, 1455 cm^{-1}. UV (EtOH): 246 nm (log ε, 4.41).

Reaction of 1 with 5f. A mixture of **1** (5.92 g, 20 mmol), **5f** (4.06 g, 20 mmol), and anhydrous diglyme (50 ml) was heated at 120 °C for 15 min to evolve a quantitative amount of nitrogen gas (0.45 l). After the separation of a quantitative amount of **3** (3.55 g), the filtrate was treated as usual to give a mixture of crystals and an oil. The crystals of the recovered **5f** (1.85 g) were removed by filtration, and the filtrate was chromatographed on silica gel to give a pale yellow oil **6f** (480 mg, 8%) when pet ether–benzene (5:5) was used and crystals of the recovered **5f** (1.65 g) when pet ether–benzene (4:6) was used. The oil **6f** was further purified by thin-layer chromatography, using pet ether–benzene (5:5) as the developing solvent.

6f: Found: *m/z* 293.1194. Calcd for $C_{22}H_{15}N$: 239.1204. Mass *m/z* (rel intensity): 293 (M^+, 81), 265 (7), 203 (43), 117 (100). IR (oil): 3030, 2950, 2220, 1460 cm^{-1}. UV (EtOH): 273 nm (log ε, 4.16).

Reaction of 1 with 5g. A mixture of **1** (14.80 g, 50 mmol), **5g** (11.20 g, 50 mmol), and anhydrous diglyme (100 ml) was heated at 120 °C for 15 min to evolve a quantitative amount of nitrogen gas (1.1 l). After the separation of a quantitative amount of **3** (3.55 g) by filtration, the filtrate was treated as usual to give a tarry material, which was then chromatographed on silica gel to yield crystals **6g** (3.84 g, 25%) when pet ether–benzene (7:3) was used and crystals of the recovered **5g** (6.98 g) when pet ether–benzene (6:4) was used. Recrystallization from benzene gave pure **6g**.

6g: Mp 105—106 °C. Found: *m/z* 313.1083. Calcd for $C_{21}H_{15}NO_2$: 313.1103. Mass *m/z* (rel intensity): 313 (M^+, 100), 267 (75), 253 (12), 208 (10). IR (KBr): 3030, 2960, 1540, 1460 cm^{-1}. UV (EtOH): 273 nm (log ε, 3.52).

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7) A referee has pointed out the possibility of the secondary formation of **6** via 1,5-hydrogen shifts or Berson-Willcott rearrangements in the tropylidene moiety of **8**, which, in this case, should be the initial addition product. According to the literature,[8] the quantitative proceedings of these rearrangements usually need the reaction conditions of heating at a higher temperature for longer periods than those of our reaction conditions (for example, the rearrangement of 1,3,6-triphenyltropylidene to 2,5,7-triphenyltropylidene is not completed even after heating at 121 °C for 70 h[8c]). Because of the mild reaction conditions (120 °C, 15 min) and because we detected no adduct of the **8** type, we consider **6** to be the initial addition product. We are indebted to the referee for his sugestion.

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